Matrix Effects During SIMS Analysis of the Lithium Mass Fractions of Silicate Glasses

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Matrix Effects During SIMS Measurement of the Lithium Mass Fractions of Silicate Glasses: Correction Procedures and Updated Preferred Values of Reference Materials

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This paper demonstrates that significant matrix-dependent bias occurs during the measurement of Li mass fractions by SIMS in silicate glasses. This bias is particularly evident for basaltic and ultramafic samples, where published SIMS data of reference materials shows discrepancies up to 40% compared with other measurement techniques. Matrix effects can be successfully corrected by taking into account the SiO_2 content of the analysed material. New matrix-corrected SIMS data for a suite of silicate glass reference materials are presented (glasses from MPI-DING, USGS, Smithsonian and NIST, with a range of 46–76 g/100 g SiO_2), which are on average within 4% of Preferred Values (PV) as published in the

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GeoReM database. As several PV for Li in GeoReM are biased by the inclusion of inaccurate SIMS data, updated reference values are proposed that include the new SIMS dataset presented here.

Keywords: lithium, silicate glasses, reference materials, SIMS, matrix effects.

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Lithium has the lowest atomic weight of all metals in the periodic table and an important trace element in the Earth's crust and mantle. It is incompatible during partial melting and is therefore enriched in the crust (21 μg g^{-1}, Rudnick and Gao 2014) compared to the mantle (1.6 μg g^{-1}, Palme and O'Neill 2014). As its ionic radius is close to that of Mg^{2+}, it is relatively compatible in ferromagnesian minerals compared to other alkali metals (Brenan *et al.* 1998, De Hoog *et al.* 2010). Lithium is an important geochemical tracer and due to its high diffusion rate it is increasingly used in geospeedometry (e.g., John *et al.* 2012). As for all elements, accurate measurement of its mass fraction in geological materials is essential for its successful application in geochemical studies.

SIMS (secondary ion mass spectrometry; also known as *ion microprobe*) is an *in situ* technique particularly suitable for the determination of Li due to its efficient ionisation during ion sputtering as well as low instrumental backgrounds, which may hamper other techniques such as LA-ICP-MS. The quality of quantitative SIMS data depends amongst others on the availability of well-characterised, homogenous and easily available calibration materials. Several suites of silicate glass reference materials with Li data are available, including the NIST glass SRM 610–617 (Kane 1998), the MPI-DING glasses (Jochum *et al.* 2000) as well as USGS basaltic glasses GSA1-G, GSC1-G, GSD1-G and GSE1-G (Guillong *et al.* 2005). For analytes that were not certified during development of these reference

materials, geoanalysts rely increasingly on compilations of published geochemical data (e.g., Pearce *et al.* 1997, Jochum *et al.* 2006, 2011), including the online database GeoReM (Jochum *et al.* 2005a). SIMS data is included in most compilations for *in situ* reference materials. However, a well-documented drawback of SIMS is its relative sensitivity to matrix composition (Shimizu and Hart 1982, Eiler *et al.* 1997), leading to so-called matrix effects (matrix-induced fractionation), and therefore the major element composition of the calibration materials should match that of the unknowns as closely as possible. The magnitude of matrix effects differs per element and is dependent on the instrumental setup used during the measurement process. In the case of Li, it has been demonstrated that matrix effects have a significant effect on quantification of Li mass fraction in silicate glasses and minerals (Ottolini *et al.* 1993, Ottolini and Hawthorne 1999) and isotope ratio determination of Li in silicate glasses (Kasemann *et al.* 2005) and olivine (Bell *et al.* 2009). A procedure to reduce matrix effects is to apply energy filtering of the secondary ions, as their energy distribution is different in different matrices. In general, matrix effects are found to be less for high-energy ions, as the largest variations in the energy distribution occur at low energy (e.g., Ottolini *et al.* 1993 for Li in silicates). Nevertheless, for Li matrix effects have been shown to persist even when using energy filtering (Ottolini *et al.* 1993).

This paper aims to (1) quantify matrix effects during Li elemental analysis by SIMS in commonly used silicate glass reference materials, and to (2) evaluate how current 'preferred values' for in GeoReM are biased by inclusion of uncorrected SIMS data, which affects low SiO_2 (ultramafic) glasses in particular. A calibration strategy to correct for matrix effects is presented and new preferred values for Li for several reference materials are proposed.

Analytical procedure and data treatment

Mass fractions of lithium and several additional trace elements were measured using a Cameca IMS 4f instrument at the Edinburgh Ion Microprobe Facility. A primary beam of $^{16}O^-$ with a net impact energy of 14.5 keV was focussed onto gold-coated samples containing polished pieces of reference material glasses. Spot size was about 10 by 15 µm. High energy (75 ± 20 eV) secondary ions sputtered from the sample surface were extracted and

accelerated into the mass spectrometer and counted using a single electron multiplier with a dead time of 14.5 ns. The instrument was operated at low mass resolution (M/ΔM *ca*. 400) using a 25-µm image field to maximise transmission. Prior to analysis the target area was cleaned using a 2-min pre-sputter with a 20 µm raster size at measurement beam conditions.

Silicate glass reference materials were analysed in three measurement sessions on 26 November 2012 (Session 1), 25 January 2016 (Session 2) and 8 December 2017 (Session 3), respectively. The sessions mainly differed in primary beam current (10 nA during Session 1 and 5 nA during Sessions 2 and 3). Despite long gaps between sessions, instrument sensitivity was virtually identical, being 0.09–0.10 counts/s nA^{-1} $(\mu g\ g^{-1})^{-1}$ for ^{30}Si for the GSD1-G reference material for all three sessions. During Session 1 the following mass stations were measured sequentially (total measurement time per mass station in seconds in brackets, split into five cycles): $^{7}Li^{+}$ (25 s), $^{9}Be^{+}$ (25 s), $^{11}B^{+}$ (25 s), $^{19}F^{+}$ (50 s), $^{30}Si^{+}$ (15 s) and $^{35}Cl^{+}$ (50 s). During Session 2, $^{26}Mg^{+}$ (15 s) was measured instead of ^{9}Be. During Session 3, $^{39}K^{+}$ (10 s) and $^{47}Ti^{+}$ (15 s) were added. Only data for mass stations $^{7}Li^{+}$ and $^{30}Si^{+}$ are reported here. Internal precision (defined as the standard error of the mean of five repeat cycles expressed as $^{7}Li/^{30}Si$) of individual Li measurements were generally < 1%. Signal drift with time was monitored by repeat measurements of Li mass fraction in NIST SRM 610 and/or GSD1-G reference materials, but no drift was observed in any of the sessions. Detection limit of Li is < 0.2 ng g^{-1} based on analysis of ultrapure Suprasil® 3002 quartz glass, indicating that $^{6}LiH^{+}$ and $^{28}Si^{4+}$ interferences on $^{7}Li^{+}$ were negligible or fully resolved and that any Li contamination on the surface was effectively removed during the pre-sputter routine.

To derive mass fractions from secondary ion signals, net count rates of the measured isotope of the target element are typically normalised to those of an internal standard element, i.e., an element with known or independently measured mass fraction. For silicates, this element is most commonly Si. For each glass reference material a *relative ion yield* (RIY) for Li compared with Si was calculated: $(^{7}Li_{abun} / {}^{30}Si_{abun}) / (X_{Li}^{STD} / X_{Si}^{STD})$, where X^{STD} is the mole fraction in the RM, and $^{7}Li_{abun}$ and $^{30}Si_{abun}$ are count rates corrected for isotope abundance. Silicon is also the element that is most variable in terms of mass fraction (46–76 g/100 g SiO_2 for the glasses presented in this study), and therefore the first to be evaluated

when assessing matrix effects. If matrix effects are absent, the RIY will be the similar for all reference materials (within analytical uncertainty), whereas if the RIY varies systematically with SiO_2 mass fraction, a correction for matrix effects will need to be applied.

In principle, RIYs should be calculated using Preferred Values (PV) as compiled in the GeoReM database. However, as the preferred values in GeoReM include SIMS data, using these PV may lead to an underestimate of the true matrix-induced bias (as demonstrated below). Therefore, RIYs were calculated using published values in the GeoReM database (Application Version 22, November 2017, see next section for details) with exclusion of all SIMS data (referred to as 'PV excl. SIMS' in the remainder of this manuscript; see electronic supplement for compilation).

Glass reference materials

Pieces of glass from the silicate reference materials listed below were mounted in small epoxy-filled holes within 25 mm wide aluminium disks. The mounts were ground down to expose the glass and then polished with diamond slurry down to 1 µm grit. Prior to analysis the mounts were cleaned with an organic solvent and de-ionised water, and coated with a *ca*. 20 nm thick Au layer to prevent charging during ion sputtering.

MPI-DING glasses

These glasses were made from undoped natural rock powders at the Max Plank Institute, Germany (Jochum *et al.* 2000) and span a wide range of compositions (komatiite-rhyolite, 46–76 g/100 g SiO_2). Current preferred values (PV) for Li are based on the data compilation from Jochum *et al*. (2006). For most PV, this included one to two solution ICP-MS values, three to four SIMS values and five to six LA-ICP-MS values, for which unweighted means were calculated. These values are listed as certified values in GeoReM (as opposed to less reliable information values), as they were obtained from at least three different laboratories using at least three independent techniques that were in statistical agreement.

NIST SRM 610, 612 and 614

These alkali-rich silicate glasses prepared by Corning Glass Works for the National Bureau of Standards (now NIST) were doped with nominally 500, 50 and 5 μg g^{-1} trace elements of most elements in the Periodic Table (Kane 1998). Many compilations that include Li data exist, including five for NIST SRM 610, ranging from 468–488 μg g^{-1} except one value of 428 μg g^{-1} (as listed in GeoReM; Jochum *et al.* 2005a); four for NIST SRM 612 with values ranging from 40–42 μg g^{-1}, and a recent compilation value of NIST SRM 614 of 1.69 μg g^{-1} (Jochum *et al.* 2011).

USGS glasses (GSA-1G, GSC-1G, GSD-1G and GSE-1G)

These synthetic glasses of basaltic composition were prepared from glasses with broadly andesitic composition made by Corning Glass Works (Myers *et al.* 1976, Wilson and Taggart 2000) and were doped with nominally *ca*. 0, 5, 50 and 500 μg g^{-1} of a wide range of trace elements as well as several major elements (Guillong *et al.* 2005). Lithium data is relatively scarce; the most recent compilation (Jochum and Stoll 2008) did not include GSA-1G, and only GSD-1G has a third technique required for calculation of reference values. Note that in GeoReM Li data for these reference materials is indicated as 'mean of new data' only.

USGS glasses (BCR-2G, BHVO-2G, BIR-1G)

These natural, undoped glasses of basaltic composition were prepared from powder reference materials BCR-2, BHVO-2 and BIR-1, respectively, by melting at 1540 °C under nitrogen atmosphere (Wilson and Taggart 2000). No published compilation exists for Li (the Jochum *et al.* 2005b compilation does not contain Li data), but GeoReM contains PV based on averages for different analytical techniques in the database (Jochum and Stoll 2008). For BCR2-G a large dataset now exists, including more than sixty values and three different techniques. Note that in GeoReM Li data for these reference materials is indicated as 'mean of new data' only.

Smithsonian glasses (VG-2, VG-A99, VG-568)

These are natural glasses prepared for use in electron microprobe laboratories (Jarosewich *et al.* 1980) and have not routinely been analysed for trace element mass fractions. A single LA-ICP-MS value for Li in VG-2 of 7.2 μg g^{-1} exists (Jenner and O'Neill 2012).

Results and discussion

Quantification of matrix effects

A summary of the data from this study is presented in Table 1, whereas all individual data from the three measurement sessions is listed in online supporting information Appendix S1. Intermediate precision of the mean of the three measurement sessions expressed as 1*s* is generally better than 5% and often close to 2% (Table 1). RIYs for Li were calculated for all measured silicate glass reference materials (Table 1) and those measured in all three sessions were plotted against SiO_2 (Figure 1). A clear correlation with SiO_2 mass fractions can be seen, with the RIYs increasing from 0.8–1.0 at 46 g/100 g SiO_2 to 1.4-1.6 at 76 g/100 g SiO_2. Hence, in silica-rich matrices, the RIY for Li is *ca*. 40% higher than in silica-poor matrices. For comparison, B measured in the same measurement procedure as Li shows no such change in RIY (Figure 1), demonstrating the absence of matrix-induced bias for this element.

<Table 1 here>

Matrix effects during Li determination in silicate glasses are not unique to our instrument, but has also affected published SIMS data from other laboratories. This can be demonstrated by comparison of SIMS data compiled in GeoReM with data from other measurement techniques (solution ICP-MS and laser ablation ICP-MS; PV excl. SIMS). When plotting the relative difference between PV and the average value for each technique against the SiO_2 content of each RM, significant differences are apparent, which are largest at low SiO_2 (Figure 2). The effect is strongest for SIMS, but a small opposite effect can be seen for sol-ICP-MS and LA-ICP-MS. It is likely that the latter is due to inclusion of SIMS data in the preferred values compiled in GeoReM (Jochum *et al.* 2006), as this will lower the average from which PV are calculated. The effect is consistent with high-SiO_2 reference materials, such as NIST SRM 610, being used for SIMS calibration, as was the case for most SIMS data in GeoReM (Jochum *et al.* 2000, 2006, Kasemann *et al.* 2005).

<Figure 1 here>

The observed trends do not prove it is the SIMS data that is offset, as it could be the laser ablation and solution ICP-MS data instead. However, considering (1) that matrix effects correlating with SiO_2 contents have been demonstrated for Li in other matrices and/or during isotope ratio analysis (Ottolini *et al.* 1993, Ottolini and Hawthorne 1999, Kasemann *et al.* 2005, Bell *et al.* 2009), (2) it is shown here that Li shows a matrix effect whereas B does not, and (3) ICP-MS is generally considered to be relatively insensitive to matrix effects (e.g., Sylvester 2008), it is most likely that SIMS data in GeoReM for Li is inaccurate. Since SIMS data for Li in GeoReM was obtained from four different laboratories, it appears that matrix effects for Li are inherent to SIMS analysis.

<Figure 2 here>

Correction of matrix effects to improve accuracy of SIMS data

As the sputtering and ionisation process during SIMS is poorly understood and no accurate physical model exists that may explain observed matrix effects, the correction of this effect is by necessity purely empirical (Eiler *et al.* 1997). During SIMS trace element analysis, quantification is often done using working curves. Such working curves are most conveniently expressed as $^{7}Li/^{30}Si$ x SiO_2 (g/100 g) vs. Li (µg g^{-1}), as the slope of such a plot is linearly related to the Li mass fraction of the calibration materials. However, due to matrix effects one may get quite different results depending on the SiO_2 contents of calibration materials used (i.e., high-SiO_2 RMs will results in a different slope than low-SiO_2 RMs). Therefore, here we adopted a different approach. $^{7}Li/^{30}Si$ of calibration materials are used to calculate RIYs for the reference materials, which are then plotted against their SiO_2 mass fraction. This results in a positive trend, the slope and intercept of which was used to calculate a corrected RIY for each SiO_2 mass fraction (Figure 1, see Appendix S2 for details of calibrations of individual sessions).

This corrected RIY is used to calculate Li mass fractions of RMs and unknowns using the following expression:

$$Li\ (\mu g\ g^{-1}) = ({}^{7}Li/{}^{30}Si \times m_{Li}/a_{7Li} \times a_{30Si} \times 10^{4}/m_{SiO_2}) / (slope + intercept / SiO_2) \quad (1)$$

where ^{7}Li and ^{30}Si are secondary ion count rates of ^{7}Li and ^{30}Si in the unknown, m_{Li} = atomic weight of Li (6.941) , m_{SiO_2} = molecular weight of SiO_2 (60.08), a_{7Li} = abundance of ^{7}Li (92.4%), a_{30Si} = abundance of ^{30}Si (3.09%) and SiO_2 is the SiO_2 mass fraction (g/100 g) of the unknown, and *slope* and *intercept* represent the change in RIY (Li/Si) with SiO_2 as determined in Figure 1.

If calibration materials were measured more than once during a session, their average RIY was used in the regression (of RIY vs. SiO_2 mass fraction). In addition, to avoid bias between sessions, only calibration materials that were measured in all sessions were used in the regression. As discussed earlier, we used PV excl. SIMS for calibration instead of PV, to avoid any bias of SIMS data uncorrected for matrix effects in the GeoReM database. The procedure results in effective removal of matrix effects as a function of SiO_2 mass fraction (Figure 3A).

<Figure 3 here>

Matrix-corrected Li data for all silicate glass reference materials measured in this study are presented in Table 1. The bias of this dataset from GeoReM PV is much reduced, averaging only 4%, compared with 12% before matrix correction. The reduced bias is also visible as much reduced scatter in a plot of measured Li versus Li PV (Figure 3B). Current values for NIST SRM 610, 612 and 614 are not affected by matrix effects, as published SIMS data for the latter two was generally calibrated using the first and all have the same matrix. SIMS data presented here for NIST RMs agrees well with compiled data (Jochum *et al.* 2016), despite the RMs having a rather unusual, high alkali matrix composition, proving that matrix effects are effectively removed by using a matrix correction based on SiO_2 content alone.

Updated preferred values

Using the new SIMS data presented here, and including new data added to the GeoReM database since publication of compilation values in 2006–2008 (GeoReM version 22, November 2017), updated preferred values for Li in silicate glasses were calculated (Table 2, see Appendix S3 for compilation). We followed the IAG protocol for certifying reference materials (Kane *et al.* 2003) as adopted in previous compilations of MPI-DING (Jochum *et al.* 2006) and NIST SRM 610–617 glasses (Jochum *et al.* 2011), and we refer to the latter publication for details of the procedures. In summary, to derive new PV we calculated an unweighted mean with all available data in the GeoReM database. Outliers were identified using the Horwitz function, which calculates a *z*-score for each mass fraction. Data with *z*-scores < -2 or > 2 were excluded. All previously published SIMS data were also excluded, independent of their *z*-score, as we demonstrated above that these are variably inaccurate. New PV can be considered Reference Values if they were derived from at least three different measurement techniques by ten or more laboratories, or at least fifteen laboratories if only two measurement techniques were available (Jochum *et al.* 2011). If data included in the PV did not meet these criteria, they were assigned Information Value. The new PV are accompanied by uncertainties (*U*) at the 95% confidence level, with $U = t * u$, where t = is Student's *t*-distribution factor calculated based on the number of values (N) used for the calculation of each PV, and u^2 = variance of all available data. No attempt was made to characterise sample homogeneity, as previous compilations identified no inhomogeneity issues for lithium and because two of the measurement techniques are micro-analytical techniques, so any heterogeneity will be included in the variance of the mean. Laboratory bias was deemed to be negligible, as agreement between the three different techniques (SIMS, sol-ICP-MS, LA-ICP-MS) was generally excellent (standard deviation < 5%, except for GOR128-G and BHVO-2G 6%).

Differences between new and old PV are significant for ultramafic glasses GOR128-G and GOR132-G, which increase by 4% and 7% relative, respectively, and basaltic glasses KL2-G and BIR1-G, which increases by 10% and 9%, respectively. Whereas the increase in PV for

ultramafic glasses is due to the updated SIMS data, the increase for BIR-1G and KL2-G is partly due to new LA-ICP-MS data added to GeoReM since the earlier compilations (Guillong *et al.* 2005, Jochum and Stoll 2008). As new PV are largely based on LA-ICP-MS data, additional SIMS data for all reference materials following the guidelines below would be beneficial, in the absence of data from more definitive measurement methods such as ID-TIMS (Jochum *et al.* 2011).

<Table 2 here>

<Figure 4 here>

Recommendations for quantification of Li mass fractions by SIMS

As reviewed above, matrix-induced bias in the analysis of Li by SIMS appears to be universal amongst SIMS laboratories. The effect is significant; for example, if the difference in mass fraction between calibration material and unknown is 5 g/100 g SiO_2, this may lead to a 5–7% bias in Li mass fraction. Therefore, it is recommended that at least three well-characterised calibration materials are used with a range of SiO_2 contents that (1) exceeds that of the unknowns and (2) is large enough to allow reliable determination of the matrix effects correction factor. It may be possible to find measurement conditions that reduce matrix effects, as preliminary work at our laboratory has shown that reducing energy filtering reduces matrix effects for Li. However, this may lead to unwanted effects for other elements in the measurement procedure, so cannot be generally recommended.

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Supporting information

The following supporting information may be found in the online version of this article:

Appendix S1.
Appendix S2.
Appendix S3.

This material is available at:

https://onlinelibrary.wiley.com/doi/10.1111/ggr.XXXXX/abstract (This link will take you to the article abstract).

Figure captions

Figure 1. Relative ion yields (RIY; see text for definition) of Li and B relative to Si, calculated for each glass reference material and plotted against its SiO_2 mass fraction, for each of the three measurement sessions included in this study. The RIY of Li strongly increases with SiO_2 mass fraction of the sample, i.e., exhibits strong matrix-induced fractionation, whereas no such trend is apparent for B.

Figure 2. Deviation of means (large circles) and all individual values (small circles) of compiled GeoReM reference material data from the current Preferred Values in GeoReM (Jochum *et al.* 2006) divided by measurement technique (SIMS, solution ICP-MS and LA-ICP-MS, respectively) and plotted against the SiO_2 mass fraction of each reference material. Note increased deviation of SIMS data from PV for SiO_2-poor glasses.

Figure 3. (a) Variation of measured Li mass fractions in reference glasses listed in Table 2 vs. SiO_2 mass fraction for concentrations uncorrected for matrix effects (blue circles) and corrected for matrix effects (orange circles). Error bars are based on one standard deviation of the three different sessions in which the reference glasses were measured. (b) Plot of measured Li mass fractions vs. Li PV excl. SIMS for matrix-corrected (orange circles) and uncorrected (blue circles) mass fractions. Note that scatter is much reduced for matrix-corrected mass fractions. Error bars are based on standard deviations of three repeats for SIMS data from this study and standard errors of the mean of compiled GeoReM values, and are generally smaller than symbol size.

Figure 4. Comparison of new and old PV including 95% uncertainty limits for MPI-DING and USGS reference materials. Old PV are generally lower due to inclusion of matrix-biased SIMS data and fall near or even outside the lower 95% CL of the new PV for most reference materials. Note that 95% CL are greatly reduced due to new data in GeoReM and exclusion of matrix-biased SIMS data.

Table 1. SIMS measurements of Li in silicate glass reference materials

	SiO_2 (g/100g) [a]	mean $^{7}Li/^{30}Si$	mean RIY [b]	mean Li (µg/g)	1s [c]	N [d]	cal. [e]	*Li PV excl. SIMS* [f]	*diff.* [g]
MPI-DING glasses									
GOR128-G	46.1	0.0053	0.86	9.9	±0.2	5	x	*11.1*	*-11%*
GOR132-G	45.5	0.0050	0.92	9.4	±0.4	4	x	*9.6*	*-2%*
KL2-G	50.3	0.0031	1.13	5.8	±0.1	6	x	*5.4*	*8%*
ML3B-G	51.4	0.0024	1.06	4.6	±0.1	5	x	*4.6*	*0%*
T1-G	58.6	0.0107	1.20	20.0	±0.2	6	x	*20.2*	*-1%*
StHs6/80-G	63.7	0.0105	1.27	20.0	±0.2	4	x	*20.4*	*-2%*
ATHO-G	75.6	0.0145	1.48	28.0	±0.3	6	x	*28.8*	*-3%*
USGS glasses									
GSE-1G	53.7	0.2460	1.16	450.7		1		*440.8*	*2%*
GSD-1G	53.2	0.0248	1.16	46.6	±0.9	10	x	*43.7*	*7%*
GSC-1G	52.6	0.0034	1.15	6.2		1		*6.0*	*3%*
GSA-1G	51.2	0.0010	1.18	1.8		2		*1.7*	*9%*
BCR-2G	54.4	0.0050	1.13	9.3	±0.2	11	x	*9.3*	*0%*
BHVO-2G	49.3	0.0026	1.12	5.0		2		*4.5*	*12%*
BIR-1G	47.5	0.0018	1.00	3.4		2		*3.3*	*2%*
VG-2	50.6	0.0040		7.3		1		*(7.2)*	*2%*
VG-A99	51.0	0.0112		21.2		4			
VG-568	77.0	0.0326		63.1		1			
NIST glasses									
SRM610	69.7	0.2522	1.45	481.7	±6.2	7	x	*468.0*	*3%*
SRM612	72.1	0.0198	1.37	38.0		1		*40.2*	*-5%*
SRM614	72.1	0.0008	1.36	1.6		1		*1.7*	*-6%*

[a] SiO_2 from GeoReM database; [b] relative ion yield (Li/Si) as used for matrix correction calculation, calculated from $^{7}Li/^{30}Si$ and Li PV excl. SIMS; [c] standard deviation based on at least three measurement results from three different measurement sessions; [d] N represents number of repeat measurements of each calibration standard; [e] The marked standards were included in the working curve and matrix effect correction. [f] Preferred Values compiled from GeoReM with the exclusion of

SIMS data (used to calculate RIY). Value in parentheses for VG-2 represents a single GeoReM entry. [g] Values in this column indicate the relative offset in percent between measured SIMS value and PV excl. SIMS.

Table 2. Compiled Li data from GeoReM and updated Preferred Values

	Li (µg/g)					N [d]	Type of data [e]	**Li (µg/g)**		
	SIMS (this study)	sol-ICPMS [a]	LA-ICPMS [a]	**PV [b]**	U (95% CL) [c]			old PV [f]	U (95%CL) [g]	New/ Old PV
	mean ± s (N)									
MPI-DING glasses										
GOR128-G	9.9 (1)	9.9±0.2 (2)	11.0±1.0 (10)	**10.7**	0.6	13	RV	10.4	1.7	4%
GOR132-G	9.4 (1)	9.5±0.6 (2)	9.5±0.8 (13)	**9.5**	0.4	16	RV	8.9	1.2	7%
KL2-G	5.9 (1)	5.4 (1)	5.6±0.5 (19)	**5.6**	0.2	21	RV	5.1	0.5	10%
ML3B-G	4.6 (1)	4.7±0.2 (2)	4.6±0.5 (24)	**4.6**	0.2	27	RV	4.5	0.4	4%
T1-G	20.1 (1)	19.8±0.4 (2)	20.9±1.9 (20)	**20.7**	0.8	23	RV	19.9	0.9	4%
StHs6/80-G	20.0 (1)	21.4±3.4 (2)	20.1±1.5 (19)	**20.2**	0.7	22	RV	20.7	2.3	-2%
ATHO-G	28.0 (1)	26.4±2.6 (3)	29.0±2.4 (30)	**28.8**	0.9	34	RV	28.6	1.8	1%
USGS glasses										
GSE-1G	453 (1)		443±24 (11)	**443**	15	12	IV	430	75	3%
GSD-1G	46.8 (1)	43.8 (1)	44.6±3.5 (12)	**44.7**	1.9	14	RV	43	9	5%

GSC-1G	6.2 (1)		6.1±0.4 (3)	**6.1**	0.5	4	IV	5.9	0.8	4%
GSA-1G	1.8 (1)		1.7±0.1 (3)	**1.8**	0.2	4	IV	1.7	0.2	5%
BCR-2G	9.4 (1)	9.3±0.7 (6)	9.4±0.8 (71)	**9.4**	0.2	78	RV	9.2	0.7	2%
BHVO-2G	5.0 (1)	4.6 (1)	4.5±0.5 (24)	**4.5**	0.2	26	RV	4.4	1.9	3%
BIR-1G	3.4 (1)		3.3±0.3 (14)	**3.3**	0.2	15	RV	3.0	1.6	9%

[a] Values compiled from GeoReM with N indicating number of entries in database excluding outliers (see Electronic Appendix 3); [b] Newly proposed Preferred Values incl. SIMS data from this study, unweighted mean of all results; [c] Uncertainty (U) at 95% confidence level; [d] number of laboratory means; Reference Value (RV) of Information Value (IV) dependent on number of techniques and laboratories (see text for details) [f] Preferred Values as listed in GeoReM (version 21, 05/01/2016), derived from Jochum and Stoll (2008); [g] Uncertainty (U) at 95% confidence level as listed in Jochum et al. (2006) for MPI-DING glasses, for USGS glasses U was calculated based on data from the original compilation as listed in GeoReM (detailed in Appendix 3).